P3 Final Report

1. Background and Problem Statement

This project proposed a single solution to simultaneously solve two distinct environment problems, petroleum based plastics and wastewater treatment. The project developed a fermentation technology that converts wastewater biosolids into biodegradable plastic. It looked at bioplastic produced by some waste consuming bacteria as an opportunity to create a new way of reducing biosolids at treatment plants and a new way of creating plastics that don't accumulate in the environment.

Wastewater treatment plants (WWTPs) struggle to remove biosolids for technical, systemic, and economic reasons. A typical WWTP immediately confronts a barrage of technical challenges around biosolids: converting soluble contaminants into insoluble, convincing suspended solids to settle out, converting organic solids ultimately into methane, and drying, transporting, and storing everything that doesn't convert to gas. They typically spend at least 40% of their budget on treatment of biosolids. Additionally, municipal WWTP's are also facing the mounting realities of population growth. Their respective cities are growing faster than planned, pushing more waste down the pipe and reducing available landfill for solids storage. WWTP processes are under more health and environmental scrutiny in terms of air pollution, CO_2 production, nitrogen and phosphate leaching, pathogen removal, etc. Wastewater facilities around the world grapple with the need for more capacity and cleaner technology all the while their budgets are being cut in a recessionary economy, and the typical 40-60 year old infrastructure they rely upon is coming apart beneath them.

Cost mitigation technologies such as biogas and fertilizer production from solids have helped in some cases, but often fall short of expectations after maintenance and logistics are factored in. The costs of producing a product from waste must be covered by the return on the product. Fertilizer and biogas are both sold for less than $250 per ton. The conversion of biosolids to higher value products like bio-plastics has the potential for creating a more viable sustainable system of solids reduction.

Current methods of plastic production are energy intensive, capital intensive, polluting, and tied to the volatile markets of oil and food. The overwhelming source of production (> 99%) is petroleum based. About 5% of global crude oil is converted to plastic, and nearly that much again is used as the energy input to drill, transport, refine, fraction, polymerize, process, mold or extrude, and then place plastic goods in the market place. This industrial train of activity requires an immense amount of infrastructure including oil wells, pipelines, refineries, chemical processing plants, plastic processing plants, and distribution networks. These processes are renowned for their efficiency (particularly upstream processes such as refining), but given their global throughput the greenhouse gas emissions are significant. The nascent bioplastics industry is considerably less efficient in material and energy usage and impacts other environment systems as seen by the eutrophication of bodies of water. Moreover, the current processing of plastic despite its associated costs –capital, energy, environmental- is highly dependent on the price of

oil (price of food for crop plastics) and are therefore captive to the volatility within the market.

The proposed method of bioplastic production replaces the effort and impacts of fossil fuel usage with biosolids usage. Biosolids are already aggregated and accessible. The conversion to plastic is accomplished with bacteria and fermentation in place of complex refineries and chemical plants. The introduction of greenhouse gases is negligible as some of the CO_2 and CH_4 normally generated from biosolids treatment is instead converted into a useable commodity. Additionally, this alternative could start to loosen the hard fast knot currently binding oil and plastic prices.

The most egregious environmental consequence of petroleum plastics is not from their production, but from their end of life which requires some form of accumulation. Eighty-five percent of post consumer plastic goes to land fill where it requires thousands of years to break down. Additionally, millions of tons of plastic spill into the oceans each year and work their way into marine food chains disrupting ecosystems. This trash plastic as an environmental threat is growing and necessitates a sustainable alternative. Plastics that are renewable and biodegradables offer the best hope of a solution for people, prosperity, and the planet.

2. Purpose, Objectives, Scope

The purpose of this project was to acquire a wastewater site as a source of biosolids, to demonstrate polyhydroxylalkanoate (PHA) bioplastic from biosolids technology by building and characterizing a pilot plant, and assess the feasibility and benefits of adopting this technology.

3. Data, Outputs, Outcomes, Findings

Site Sourcing

Locating our research on site at a wastewater plant proved less reasonable than simply shipping biosolids from the site to our lab. By not locating at one particular site, we were able to experiment with biosolids from several wastewater treatment plants and gain a better understanding of site variability.

Construction of 45 liter reactor

To establish our first proof of concept, two 45 liter batch reactors were constructed to simulate the anaerobic and aerobic processes commonly found at treatment plants. Acrylic was chosen as the reactor material for its inert and transparent properties. The reactors were constructed with high length to diameter (L/D) ratios to let us observe the effects of settling, a phenomena distinctly observed in wastewater treatment as the population that survives (is recycled) is that which settles to the bottom of the secondary clarifier. Mixing was accomplished with an impeller, but required a relatively high torque for biosolids. The aerobic reactor was aerated with a single 9 inch ceramic aeration stone. Probes were used to monitor temperature, dissolved oxygen, and pH.

Acid Phase Digestion

Compared to the process typically found at waste water treatment plants, digesting solids for fatty acid production requires similar but distinct processing conditions than those used for methane production. Methanogenesis, (biogas) production, necessitates that complex constituents are first broken into acids before conversion to gas, (see Fig. 1).

The cascade of bioreactions that lead to methane includes a step of fatty acid production. This step typically peaks at a 2-5 day residence time and is occasionally used as a preliminary step to digestion where it is called acid phase digestion or APD. APD as a continuous acid production process achieves a steady state pH of 5.5-6 (lower pH is inhibiting) and a native population that self selects for acid production. Replicating this process as a batch requires a pH control mechanism and longer residence times given the un-optimized cell population. How this pH control is accomplished is important as many control systems will overshoot base addition, damaging the viability of some cell populations.

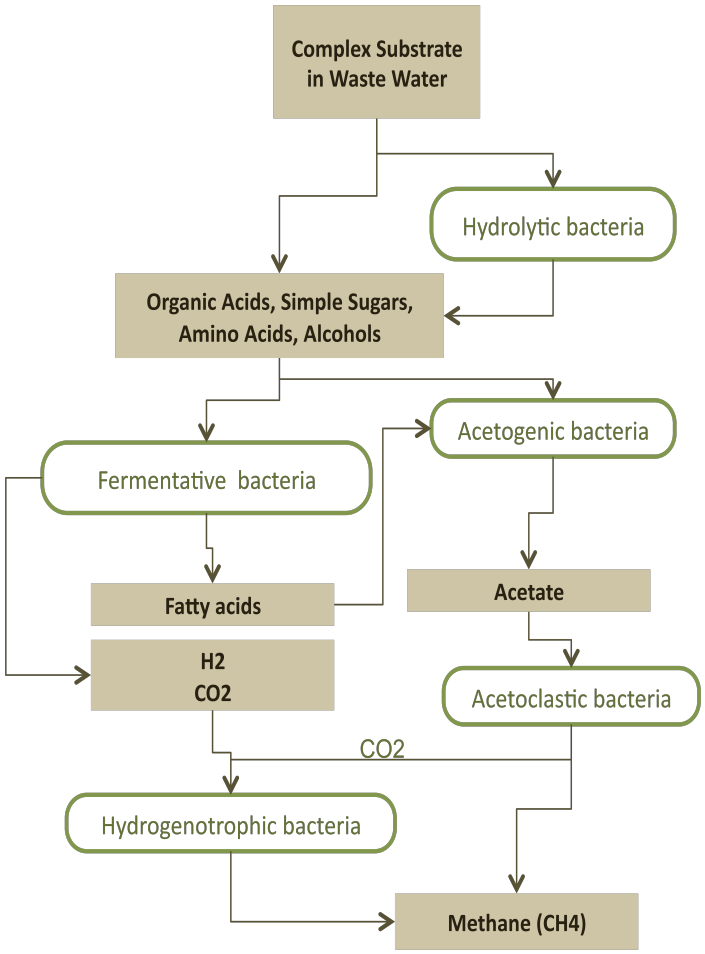

Figure 1 As described in Gerardi (2006) complex organic constituents are sequentially broken down ultimately to methane.

Sequence reactors, interesting results including some failures.

As expected, environmental factors dictate the nutrient consumption and storage rates (i.e. PHA production) of bacteria. Presently, there are three well-documented methods by which controlled environments are manipulated to favor the emergence and dominance of specific microbial species and biological behaviors (Lemos 2004, Din 2008). These three methods are the Feast Famine process where alternating feed and nutrient limitation cycles are imposed, Aerobic Dynamic Feeding (ADF) whereby feeding spikes are tied to changes in oxygen uptake of the organisms, and Aerobic/Anaerobic (AN/AE) cycling where aeration and thus dissolved oxygen is cycled.

This project implemented an array of reactors that used combinations of Feast Famine and AN/AE cycling, (Fig 2). This system used nine constructed reactors that were linked to control timers that controlled aeration and nutrient cycling over different cycle times. The process feed was filtered digestor effluent supplemented with acetate. The results from these reactors varied dramatically across the array and over time. Some resultant

populations demonstrated PHA per cell mass yields of over 30% for one given cycle and would then be overrun with fungal or protist infestation by the next cycle. After multiple runs and combinations, no clear cut cycling strategy emerged.

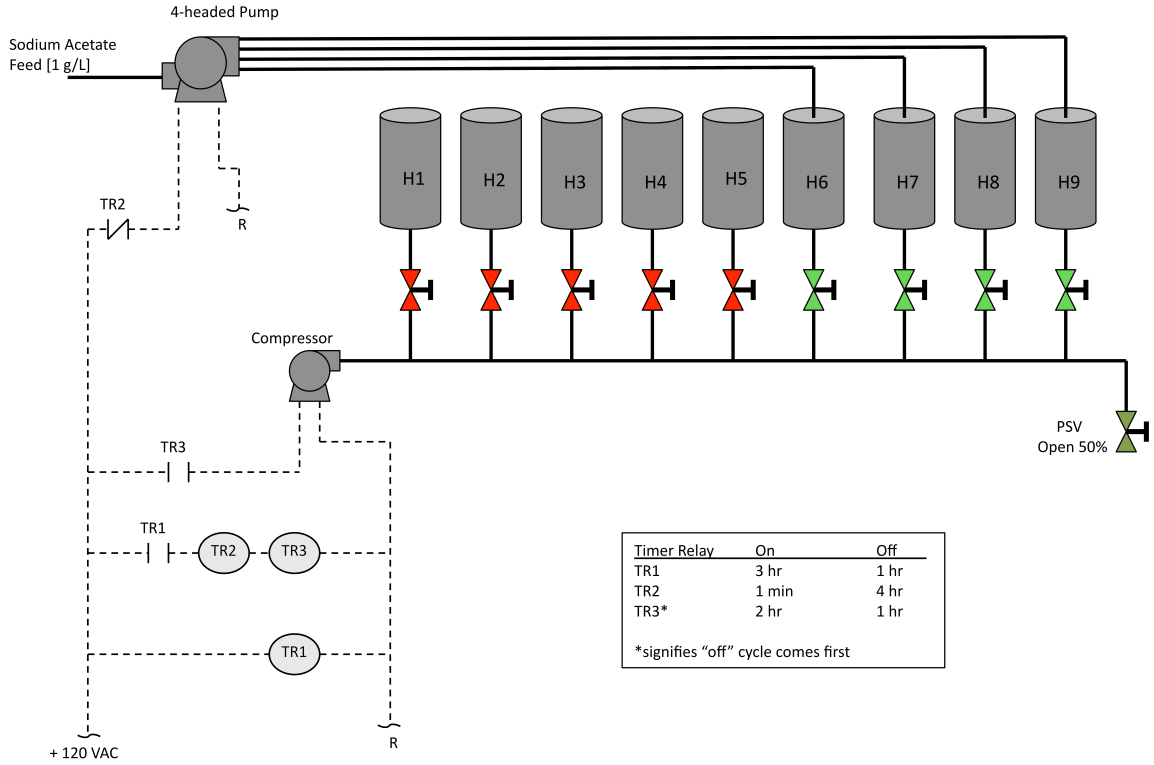

Figure 2 Equipment, reactor, and timer relay (TR) control diagram for feed and aerobic cycling of nine reactor array

To overcome this variability some of the productive species were cultured on solid nutrient media and run independently on synthetic broth. These resulting populations (species unknown) gave more consistent yields of more than 15% by dry cell mass when run within the 45 liter pilot reactor.

Difficulty of analysis,

The samples were analyzed for PHA content using gas chromatograph and a derivatization process similar to Braunegg et al. 1973 and Satoh et al. 1992. This analysis requires that the sample cells are no longer viable (or they consume the PHA bioplastic), that the depolymerase enzymes are no longer active, that the cells are lysed, and that a complete or known hydrolysis conversion occurs to give quantitative monomer peaks within the chromatogram. None of these issues is adequately addressed in literature. It was found that alkaline driven lysis can saponify ester bonds in PHA, bleach lysis is consistently incomplete, organic separation prevents water transfer and thus hydrolysis, propylated monomers give better partitioning than methylated monomers, and high derivatization or column temperature will produce some (but not complete) conversion to crotonic acid. Even as these variables that can either over or under represent the quantity

of PHA in the sample, carefully run GC analysis was still found to be the most reliable of methods.

Extraction

Despite the chromatogram peak indicating reasonable production of PHA, an actual chemical extraction of plastic from a reactor was wanted for proof of concept. As seen with the analysis effort, standard extraction methods were also difficult to implement. A standard lysis solution contains anionic surfactant(s) to disrupt cellular membranes. This same surfactant emulsifies traditional two phase organic/aqueous extraction systems. To overcome this emulsion a combination of salting, heat, and centrifugation was used to give complete separation of phases. The organic phase was then dosed with an excess of cold methanol anti-solvent to drop the plastic out of solution without drying large amounts of solvent. More than 70% of the predicted PHA content was recovered using this method.

4. Discussion, Conclusions, Recommendations

This project was broad in nature looking at site variability, scale-up, species selection, anaerobic processing, aerobic production, and extraction; and though not comprehensive on balance, a clear picture emerged demonstrating the potential challenges with mixed consortia, control, extraction, scaling, quality assurance, stakeholder buy-in, and product distribution. This study and others had shown that mixed culture processing, while productive, is not predictive. These systems evolve over time in complex ways and are subject contamination. PHA accumulation is one solution to the stringent environmental conditions imposed on the population, however it is not the only solution that could evolve within a reactor. For example carbohydrate storage could easily evolve to replace plastic storage. The complexity and non-linearity of the system presents unclear set-points for control and would not provide adequate process knowledge to troubleshoot problems. Likewise, product quality would be difficult to assure to end users. Moreover, the wastewater industry is not informed about or eager to enter the plastics industry, so that even if the technical hurdles could be overcome, the buy-in from WWTPs is tacit at best.

This is not to say that bio-plastic derived from waste water biosolids should be abandoned, the market potential and environmental impact justify further development; however alternative fermentation strategies and business models should be explored.

5. References

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